

Chapter 2

Gibbs and Helmholtz Energies

Abstract Some properties of the *Gibbs and Helmholtz energies*, two thermodynamic functions of utmost importance in chemistry especially for the study of the notion of activity, are recalled. The chemical potential of a species in a system, which is the pivotal notion of the chemical reactivity (most of the time entailing the notion of activity), is, indeed, a particular Gibbs energy. Hence, for example, the changes in Gibbs and Helmholtz energies accompanying a process provide us with an equilibrium criterion, at least in some experimental conditions.

In a first time, a brief recall of some properties of the entropy function is mentioned in order to grasp the significance of these two functions. Later in the chapter, for additional information, some notions concerning potential functions are also given.

Keywords Chemical potential • Entropy enthalpy • Electrochemical cell • Gibbs–Helmholtz relation • Gibbs energy • Helmholtz energy • Isolated system • Potential functions • Surroundings

In this chapter, we recall some properties of two thermodynamic functions of utmost importance in chemistry, especially for our purpose. They are the *Gibbs and Helmholtz energies*. The chemical potential of a species in a system, which is the pivotal notion of the chemical reactivity (most of the time entailing the notion of activity), is, indeed, a particular Gibbs energy (viz. Chap. 5). Hence, for example, the changes in Gibbs and Helmholtz energies accompanying a process provide us with an equilibrium criterion, at least in some experimental conditions.

Grasping the significance of these two functions requires, in a first time, to briefly recall some properties of the entropy function and, later, to summarize some notions concerning the potential functions.

2.1 Brief Recalls About the Second Principle and Entropy

2.1.1 General Points

It is a well-known fact that the knowledge of the changes in internal energy or enthalpy accompanying a process does not permit to forecast their direction nor their maximum possible extent (their “quantitativity”). The introduction of a new function turned out to be necessary to answer these questions.

The study of cyclic processes (that is to say that kind of processes according to which a system is brought back in its initial state after having been submitted to varied transformations) shows that another thermodynamic function answers the previous questions. It is the entropy function (symbol S , unity J K^{-1}) (in Greek: evolution). It is endowed with remarkable properties. It is a state function and it is extensive.

The second principle of thermodynamics is based on the existence of this function. It states that the entropy of an *isolated* system cannot do anything else than to increase during a spontaneous transformation. This is quantified by the expression

$$\Delta S_{\text{isolated syst}} > 0 \quad (\text{spontaneous process})$$

or equivalently

$$\Delta S_{U,V} > 0$$

(It is evident, indeed, that, according to the definition of an isolated system, the internal energy remains constant since heat, mechanical work, and matter exchanges with the surroundings cannot exist. The nonexistence of work exchange requires that the volume V of the system is constant.)

For a reversible process, the second principle states that in an isolated state the change in entropy is null, i.e.,

$$\Delta S_{\text{isolated syst}} = 0 \quad (\text{reversible process})$$

or

$$\Delta S_{U,V} = 0$$

The following relation

$$\Delta S_{\text{isolated syst}} \geq 0$$

is the mathematical counterpart of the most general statement of the second principle of thermodynamics. The increase of the entropy of the studied system plus the increase of entropy of its surroundings is called entropy creation.

2.1.2 Studied System, Surroundings, and Isolated System

One of the difficulties of the understanding of the entropy concept comes from the mix-up of the entropy of the studied system and of the entropy of the isolated system containing the studied one.

In a general manner in thermodynamics, in order to study a process, one may consider both the studied system and its surroundings with which it can, at first sight, exchange work, heat, and matter. The studied system plus the surroundings constitute an isolated system, *but the studied system, solely, may not be isolated.*

The important point is the following one: when a spontaneous process is occurring in the studied system, the entropy of the isolated system (studied system plus its surroundings) does obligatorily increase (except the case in which the process is reversible) according to the second principle, whereas it is not at all obligatory in case when it is not an isolated one. Hence, the studied system may exhibit an *increase or even a decrease* of its entropy during this spontaneous process.

Let us *already* mention that there exist other criteria of spontaneity than that of entropy, in particular in the case of a process at constant temperature and pressure. It is the point which will occupy us up to the end of this chapter.

2.2 Gibbs Energy

This function has been introduced by Gibbs.

The symbol of Gibbs energy is G . Its significance and use are related to an isothermal and isobaric process. More precisely, the Gibbs energy is related to a process in which the temperature and the pressure of the studied system remain equal to the temperature and pressure of its surroundings (at least at the beginning and at the end of the process provided, in this case, that during it, the surroundings remain at the constant temperature T_{ext} and pressure p_{ext}):

$$p = p_{\text{ext}} \quad \text{and} \quad T = T_{\text{ext}}$$

The Gibbs energy is defined by the expression

$$G = U + pV - TS$$

where U , p , V , T , and S are, respectively, the internal energy, pressure, volume, temperature, and entropy of the system. Its unity is the Joule J. Owing to its definition, the Gibbs energy is a state function.

The interest of the introduction of this function is the following one: it turns out that the Gibbs function may constitute a criterion of equilibrium and also of evolution specially convenient for any process at constant pressure and temperature.

Let us, for example, study the process with the aid of which we want to recover useful work (every work other than that stemming from the change in the volume of the system), starting from the system. (A good example is that of an electrochemical cell producing electrical energy which is connected to an electrical motor. The cell has the property to transform the chemical energy—coming from the two electrochemical reactions which simultaneously take place at each of both electrodes—to electrical work.) It is demonstrated in an absolute general manner that the work given to the surroundings is always weaker than the change in internal energy of the system. In other words, the Gibbs energy of the system cannot do anything else than to decrease when it supplies work to the surroundings, in any case when the process is spontaneous. Hence, we can deduce that

$$\Delta G \leq 0$$

or in differential writing

$$dG \leq 0$$

At equilibrium

$$dG = 0$$

For a system at equilibrium at given pressure and temperature, the Gibbs energy is at its minimum value.

Hence, with the introduction of the function of Gibbs energy, the criterion of spontaneous evolution of a system, that is to say that of the change in the total entropy (that of the system plus that of its surroundings—both forming an isolated system), is transformed into another one which is the criterion of the decrease of the Gibbs energy of the *studied system alone*. The latter criterion is evidently less heavy than the former and is easier to handle because it does not require the knowledge of the thermodynamic parameters defining the state of the surroundings. However, the criterion of the Gibbs energy is by far less general than that of entropy because, for its handling, it implies that the process evolves at constant temperature and pressure.

In this sense, we shall see that the Gibbs energy plays the part of a potential function (viz. paragraph 5).

The Gibbs energy function can be defined in another way. Of course, all its definitions are equivalent. For example, taking into account the fact that the enthalpy of a system is defined by the expression

$$H = U + pV$$

the Gibbs energy can also be written

$$G = H - TS$$

or

$$dG = dH - TdS - SdT \quad (2.1)$$

2.3 Some Properties of the Gibbs Energy Function

2.3.1 *Changes in the Gibbs Energy with the Pressure and the Temperature*

Let us consider the relation which expresses the enthalpy:

$$H = q + w + \mathbf{p}V$$

where q and w are the heat and the work exchanged with the surroundings during the process. For an infinitesimal transformation,

$$dH = dq + dW + \mathbf{p}dV + Vd\mathbf{p} \quad (2.2)$$

If this one is reversible and isothermal

$$dq = dq_{\text{rev}}$$

and after the second principle

$$dq = TdS$$

If, finally, the sole work done by the system is that of expansion as it is usually the case in chemistry

$$dw = -\mathbf{p}dV$$

the infinitesimal change in the enthalpy of the system becomes

$$dH = TdS - \mathbf{p}dV + \mathbf{p}dV + Vd\mathbf{p}$$

or

$$dH = TdS + Vd\mathbf{p}$$

By comparison with relation (2.1) which is a definition of the Gibbs energy

$$dG = dH - TdS - SdT$$

we find

$$dG = Vd\mathbf{p} - SdT \quad (2.3)$$

Now, let us write the total differential of G , which is a state function (viz. Appendix A):

$$dG = (\partial G / \partial T)_p dT + (\partial G / \partial \mathbf{p})_T d\mathbf{p}$$

We immediately deduce that

$$(\partial G / \partial T)_p = -S \quad \text{and} \quad (2.4)$$

$$(\partial G / \partial \mathbf{p})_T = V \quad (2.5)$$

These two equations give the variations of the Gibbs energy with the temperature and pressure.

In general, the Gibbs energy depends not only on the temperature and the pressure but also on the quantities of substance (viz. Chap. 4).

2.3.2 Gibbs–Helmholtz Equation

The Gibbs–Helmholtz equation permits, as we shall see, to know the change in an activity value with the temperature. It is obtained from the general definition of the Gibbs energy function:

$$G = H - TS$$

Substituting the entropy by its expression (2.4) into it, we obtain

$$G = H + T(\partial G / \partial T)_p \quad (2.6)$$

It can be modified into another one. We obtain an expression of the variation of G with the temperature T by the division of (2.6) by the factor T^2 . The relation found is

$$G/T^2 = H/T^2 + 1/T(\partial G / \partial T)_p$$

It is easy to check the following relation by a simple calculation of derivatives:

$$[\partial(G/T)/\partial T]_P = [T(\partial G/\partial T) - G]/T^2$$

Finally,

$$[\partial(G/T)/\partial T]_P = -H/T^2 \quad (2.7)$$

It is interesting to notice that relation (2.3) is valid, whatever the reversibility of the process is, since all the quantities which are in it are state quantities. It is the same for those which follow it. The sole existing constraint in order that all these considerations are valid is that the system must be closed.

2.4 Helmholtz Energy

It has been introduced by Helmholtz.

It is slightly less interesting in the realm of chemistry than the Gibbs energy is. The developments to which it leads are analogous to those stemming from the Gibbs energy.

It applies to a process in which the temperature T of the system is equal to that of the surroundings $T_{\text{ext.}}$ and during which its volume is constant. The Helmholtz energy A is defined by the relation

$$A = U - TS$$

It is a state function. It is extensive. It is expressed in joules.

The Helmholtz energy A is related to the Gibbs energy G by the expression

$$G = A + pV$$

Following the same kind of reasoning as that developed in the case of Gibbs energy, it is found that the physical significance of the Helmholtz energy is the following one. The value of its change is the maximal work that can produce the system in reversible and isothermal conditions. At equilibrium and at constant temperature, the Helmholtz energy function is minimal.

The difference between the Helmholtz and Gibbs energies lies in the fact that in the first case, the maximal work is equal to the sum of the useful work and of that of expansion whereas in the case of the Gibbs energy its decrease is only equal, in reversible conditions, to the useful work.

2.5 Gibbs and Helmholtz Energies, Potential Functions: Thermodynamic Potentials

We have seen that the Gibbs and Helmholtz functions give important indications on the possibilities of transformations of a system, respectively, at constant temperature and pressure and at constant temperature and volume. One knows that during a spontaneous process, these functions evolve in such a manner that their values tend toward a minimal value. By such a property, their behavior is that of potential functions, called thermodynamic potentials.

2.5.1 Potential Energy and Evolution of a Mechanical System

In order to make explicit this notion of potential function, let us recall the relation linking the potential energy and the evolution of a mechanical system.

Let us consider a material point M which moves freely in a force field deriving from a potential energy $E(x)$. A representative example is that of the gravitational field. One knows that if we initially abandon M at the point I (initial) of vertical coordinate $h(I)$ with a null speed, then it spontaneously tends to go to the F point (F: final) of minimal potential (viz. Fig. 2.1).

During its evolution, the body is getting a kinetic energy $1/2mv^2$. The constancy of the mechanical energy is written for each intermediate point of the path:

$$Mgh(I) = Mgh + 1/2 mv^2$$

where h is the coordinate of the intermediate point. The kinetic energy being obligatorily positive, we immediately can deduce that during this spontaneous evolution, the term potential energy can only decrease. Its minimum $Mgh(F)$ corresponds to the state of stable equilibrium. In I , the state of equilibrium was unstable.

Fig. 2.1 Potential energy $E = Mgh$ and the evolution of a mechanical system



2.5.2 *Entropy and Thermodynamic Potential*

Let us consider an isolated thermodynamic system evolving toward a final state (F) starting from the initial one (I). According to the second principle of thermodynamics, the system evolves in such a manner that its entropy is increasing:

$$S(F) \geq S(I)$$

When the entropy is already maximal in the initial state, it cannot increase and, moreover, since it cannot, in any case, decrease, it remains constant. Then, the system is at equilibrium. Let us, now, consider the function— S . One immediately conceives that, during the same process, it cannot do anything else than to decrease in order, finally, to get its minimal value at equilibrium. The function— S plays the same part as that played by the potential energy in the mechanical system above. It is a potential function called, since we are considering a thermodynamic system, a *thermodynamic potential*. The function— S , called negentropy, is not easy to handle for several reasons. The first one is probably due to the fact that there exist very few true isolated systems; this is the reason why other thermodynamic potentials have been conceived.

2.5.3 *Generalization: Definition of a Thermodynamic Potential*

One calls thermodynamic potential of a system submitted to some constraints a function Φ depending on the state parameters of the system and, possibly, on the external constraints such as, during the evolution of the system, it tends to take an extremal value (minimal or maximal) at equilibrium. The nature of the thermodynamic potential functions depends on the constraints imposed to the system, prevailing on the thermodynamic quantities extensive or intensive.

It is evident that, according to these considerations, the Gibbs and Helmholtz energy functions are thermodynamic potentials, at least for the conditions for which they have been established. The constraints imposed to the system are these conditions. We will again briefly evoke this notion of potential function when we shall mention the genesis of the notion of activity.

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